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ALUMINUM-CHLORINE BATTERY

**Maj George D. Brabson Jr.
Capt Armand A. Fannin Jr.
Lt Col Lowell A King
Maj David W. Seegmiller**

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13. ABSTRACT		
<p>Laboratory models of an aluminum-chlorine battery have been constructed and tested. The cells have an aluminum anode, a cathode consisting of chlorine stored on powdered graphite, and a molten aluminum chloride-sodium chloride electrolyte. The cells are normally operated as secondary cells, charging being accomplished by application of a reverse potential. Typical cells have an open circuit voltage of 2.55 volts, of which about 0.4 volt appears to be due to a concentration difference established in the electrolyte during electrical charging. Current densities as high as 0.8 ampere per square centimeter of aluminum anode surface area have been achieved. With respect to the maximum current achievable, the conductivity of the melt seems to be the limiting factor.</p>		

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CONTENTS

	<u>Page</u>
List of Illustrations	ii
Introduction	1
Description of Cells	2
Experimental Parameters	5
Experimental Results	6
Discussion	15
References	24
Bibliography	25

LIST OF ILLUSTRATIONS

	<u>Page</u>
Figure 1. Typical Laboratory Cell	3
Figure 2. Cell Number 802-13: Results of Voltage vs Current Experiment	9
Figure 3. Cell Number 802-13: Results of Charge- Discharge Experiment	10
Figure 4. Cell Number 802-23: Results of Charge- Discharge Experiment	12
Figure 5. Cell Number 802-28: Results of Voltage vs Current Experiment	13
Figure 6. Expected Voltages for Cells with and without Separators at 175°C and 600 torr	19

ALUMINUM-CHLORINE BATTERY

Introduction:

Work on electrochemical systems was begun in the Seiler Laboratory in 1964. The objective of this program is to develop advanced electrochemical power supplies characterized by high power per unit weight and high power per unit volume.

Early in the program it was decided to concentrate the efforts on the aluminum-chlorine electrochemical couple using molten aluminum chloride-sodium chloride mixtures as the electrolyte.¹ Some of the more important reasons for this decision are these:

(1) The aluminum-chlorine system has a high theoretical energy density. Taking the voltage of the aluminum-chlorine couple to be 2.2 volts,^{*} the theoretical energy density is 600 watt-hours per pound of aluminum and chlorine consumed.

(2) The aluminum electrode is capable of high current densities without polarization or passivation. In practice, current densities as high as 800 ma/cm² have been demonstrated.¹

The reactive materials are inexpensive and relatively easy to handle. Aluminum can be obtained in high purity and can be easily formed to the desired shape. Chlorine, although toxic, can be stored conveniently as a liquid below 144°C, the critical temperature.

During the initial phases of work on the aluminum-chlorine system, the principal efforts were devoted to studying the properties of pure aluminum chloride, of aluminum chloride-sodium chloride melts, and of electrodes dipping into these melts. Basic physical chemical measurements are continuing at the present time. In 1970, it was discovered that a concentration cell using aluminum electrodes and aluminum

1. L.A. King, A.D. Brown, Jr. and F.H. Frayer, "High Energy Density Electrochemical Cells," Proceedings of the Third OAR Research Applications Conference, March 1968, Vol. 1, p. J-1.

* This voltage is approximately equal to the potential measured for the reaction of aluminum with chlorine in an aluminum chloride-sodium chloride melt saturated with respect to sodium chloride; the measurement is discussed in detail on pages 17 through 21.

chloride-sodium chloride electrolytes can develop potentials as high as 0.6 volt.^{2,3,4} The Bibliography contains a complete list of publications which have resulted from the work to date.

Description of Cells:

To date, nine different cells have been constructed and tested in the laboratory. Since all the cells were similar in most respects, one cell (designated #802-13) has been selected for detailed description. The characteristics of the remaining eight cells will be described only insofar as they differ from those of Cell Number 802-13.

1. Cell Number 802-13. Cell Number 802-13 is illustrated by Figure 1.

a. Aluminum Electrode. The aluminum electrode was a 100 cm long piece of 0.032 inch diameter "Baker Analyzed" reagent aluminum wire. The electrode was formed into a spiral approximately 25 mm in diameter and was connected to the external circuit by an additional piece of aluminum wire sheathed in Pyrex^{*} tubing.

b. Chlorine Electrode. The chlorine electrode consisted of a spiral of Alpha Inorganics 3n5 0.030 inch diameter tungsten wire immersed in a mixture of finely powdered graphite and electrolyte. The spiral was formed from wire heated to redness in a gas-air flame. The oxide layer formed on the surface of the tungsten was removed electrochemically in a cell having an aluminum chloride-sodium chloride electrolyte. The electrolyte in the chlorine electrode compartment was almost completely immobilized by the graphite powder. The graphite present, 4.8 grams, constituted approximately 25 percent by weight of the graphite-electrolyte mixture. The graphite was prepared by grinding large flakes of the type typically used as a dry lubricant.

2. A.A. Fannin, Jr., L.A. King and D.W. Seegmiller, "A Lightweight High Energy Battery," Proceedings of the Air Force Systems Command 1971 Science and Engineering Symposium, 5-7 October 1971.
3. L.A. King, D.W. Seegmiller and A.A. Fannin, Jr., "Aluminum High Energy Density Concentration Cells," Air Force Research Review, No. 3, May-December 1971, p. 8.
4. A.A. Fannin, Jr., L.A. King and D.W. Seegmiller, "Chloroaluminate Equilibria in $\text{AlCl}_3\text{-NaCl}$ Melts," J. Electrochem. Soc., **119**, 801 (1972).

* Registered Trademark of the Corning Glass Works.

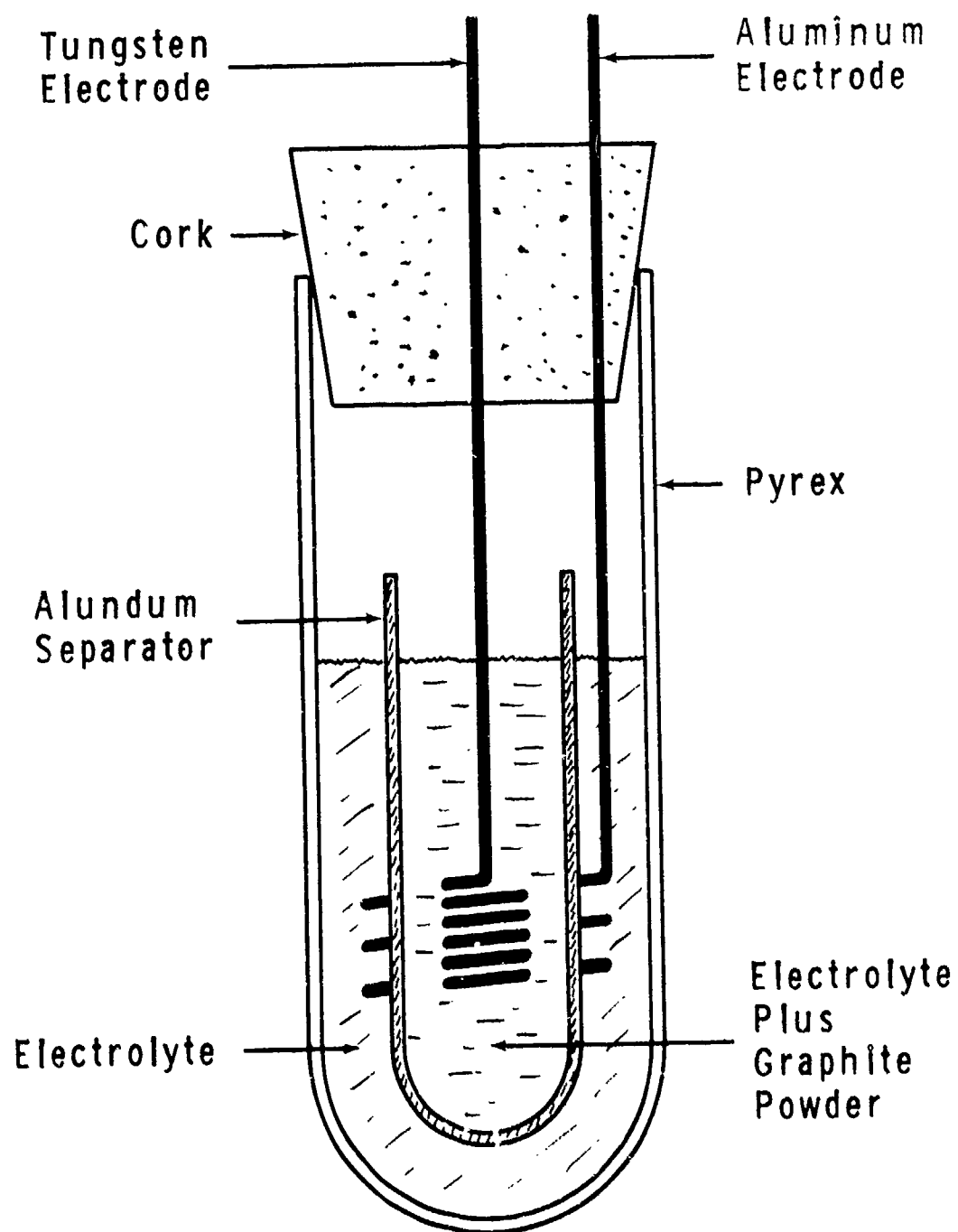


Figure 1. Typical Laboratory Cell

c. Electrolyte. The electrolyte was a molten saturated solution of sodium chloride in aluminum chloride. At the temperatures of interest, nominally 200°C, this solution contained very nearly 50 mole percent of each of the two chloride salts. The electrolyte mixture was prepared by mixing 40.0 grams of "Baker Analyzed" reagent AlCl_3 with 20.0 grams of "Baker Analyzed" reagent NaCl . The excess sodium chloride, slightly over two grams, was allowed to collect in the bottom of the cell.

d. Separator. An Alundum^{*} (porous alumina) filter thimble, porosity RA-360 medium, was used to separate the two electrode compartments. The thimble had a length of 90 mm and an outside diameter of 19 mm.

e. Assembly. The cell was assembled in a 35 mm OD, 31 mm ID Pyrex tube. The Alundum separator was supported by glass beads placed in the bottom of the cell; this arrangement prevented the separator from resting on the undissolved excess sodium chloride in the bottom of the tube. The graphite was placed inside the separator; a Pyrex wool plug, placed in the top of the separator, prevented the graphite from being spattered out of the separator during electrical charging of the cell. The tungsten coil was completely immersed in the graphite-electrolyte mixture in the chlorine electrode compartment. The entire assembly operation was conducted in a dry box.

2. Cell Number 801-11. Initially the chlorine electrode compartment of Cell Number 801-11 contained one gram of Nuchar^{**} C-150N decolorizing carbon; later one gram of graphite was added. Two current collectors were tested in the chlorine electrode compartment of this cell: a platinum foil and a 1/4 inch diameter National^{***} spectroscopic grade graphite rod (tungsten was not used in this cell). The platinum was rapidly attacked by its environment and not used again in subsequent cells. The graphite rod also was eroded by the environment.

* Registered Trademark of the Norton Company.

** Trademark of the Westvaco Corporation.

*** Registered Trademark of the Union Carbide Corporation.

3. Cell Number 801-23. Both tungsten and 1/4 inch diameter graphite rod current collectors were tested in the chlorine electrode compartment.

4. Cell Number 802-12. Initially the chlorine electrode compartment of Cell Number 802-12 contained only one gram of graphite, and a 1/4 inch diameter graphite rod current collector was used. After several cycles, 2.4 grams of the graphite rod had been eroded, giving the chlorine electrode compartment a total graphite content of 3.4 grams. At this point the graphite rod was replaced with a tungsten current collector.

5. Cell Number 802-23. Cell Number 802-23, designed to investigate the feasibility of using a chlorine trapping medium other than graphite, had 1.5 grams of Nuchar C-190N decolorizing carbon in place of the graphite in the chlorine electrode compartment.

6. Cell Number 802-28: Cell Number 802-28 had an electrolyte solution containing 40 mole percent sodium chloride.

7. Cell Number 807-12. Cell Number 807-12 had an anode consisting of a cylinder of commercial aluminum tubing with an ID of 25.5 mm and a height of 31 mm. The cell was operated at a temperature of 175°C.

Experimental Parameters:

1. Temperature. The cells, except for Cell Number 807-12, were operated at a nominal temperature of 200°C in a fused salt bath consisting of a ternary eutectic mixture of NaNO_3 , KNO_3 and NaNO_2 .

2. Electrical Charging. Electrical charging was accomplished by impressing a reverse potential on the cell. The nominal open circuit charging voltage was 3.0 volts, and was not carefully regulated.

3. Electrical Measurements. Voltage measurements were made using a voltage divider network and a calibrated strip chart recorder. The impedance of the measuring circuit was 0.5 megohm.

4. Charge - Discharge Experiments. A typical charge-discharge experiment consisted of a series of charge-discharge cycles, and followed the format indicated by Table 1.

TABLE 1. FORMAT OF CHARGE-DISCHARGE EXPERIMENTS.

Cycle Number	Length of Charging Phase (min)	Length of Discharge Phase (min)
1	1	3
2	2	3
3	4	3
4	8	3
5	16	3
6	32	3
7	64	3

In each case, the load applied during the discharge phase was the same, viz., 5.08 ohms.

5. Voltage, vs. Current Experiments. Voltage vs. current experiments were conducted by applying calibrated loads to the cell and monitoring the voltages developed under the various loads. These experiments were usually conducted using cells that had been previously charged for 16 minutes or longer.

Experimental Results:

A brief summary of experimental results is contained in Table 2.

1. Cell Number 802-13. Cell Number 802-13 gave by far the best results. Figure 2 shows the results of a voltage vs. current experiment. The fact that the data fall on a straight line leads to the conclusion that the cell behaved ideally and may be considered to consist of constant voltage source (the open circuit voltage) in series with a constant resistance (the internal resistance). With an externally applied load equal to the internal resistance, the cell developed its maximum power, 4.2 watts.

The results of a series of charge-discharge experiments with this cell are shown in Figure 3. As expected, significant improvement in the discharge performance was observed as the length of the charging phase was increased.

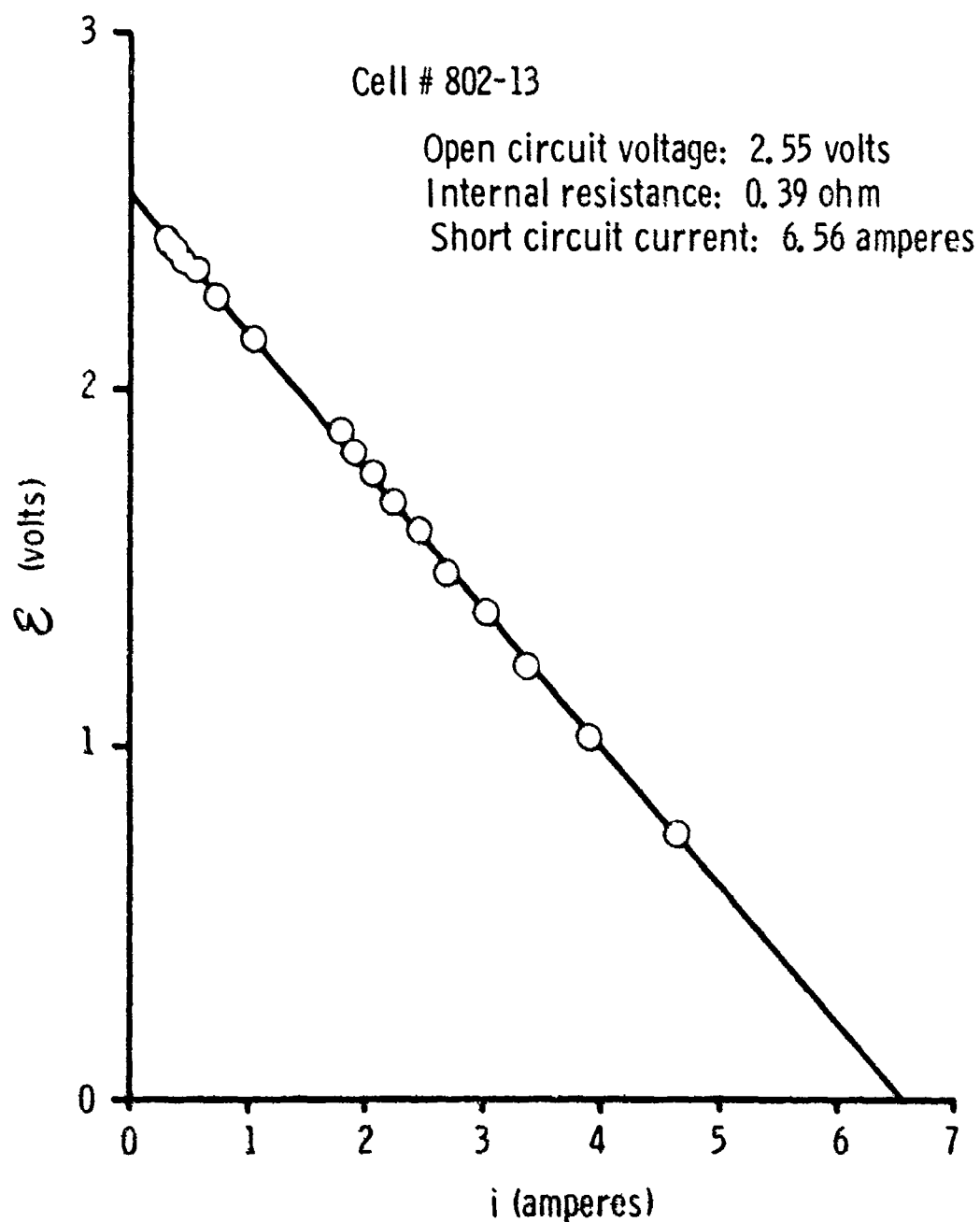


Figure 2. Cell Number 802-13: Results of Voltage vs Current Experiment

TABLE 2. SUMMARY OF EXPERIMENTAL PARAMETERS AND RESULTS

CELL NUMBER	ELECTROLYTE		CATHODE		CURRENT COLLECTOR	ALUMINUM ANODE AREA (cm ²)
	MOLE % NaCl	TOTAL MASS (grams)	TYPE OF CARBON	MASS OF CARBON (grams)		
801-11	50			None	platinum	18.4
	50		charcoal	1.0	platinum	18.4
	50		{ charcoal + graphite }	{ 1.0 + 1.0 }	platinum	18.4
	50		{ charcoal + graphite }	{ 1.0 + 1.0 }	graphite	18.4
801-23	50		graphite	6.0	tungsten	20
	50		graphite	6.0	graphite	20
802-12	50		graphite	1.0	graphite	8.1
	50		graphite	3.4	tungsten	8.1
802-13	50	60	graphite	4.8	tungsten	8.1
802-23	50	52.5	charcoal	1.5	tungsten	8.1
802-28	40	53.2	graphite	4.8	tungsten	8.1
804-9	50	52.5	graphite	5.0	tungsten	8.1
806-18	50	87	graphite	5.0	tungsten	5.4
807-12	50	90	graphite	5.0	tungsten	24.5

TABLE 2. (Continued)

CELL NUMBER	CHARGE-DISCHARGE EXPERIMENTS		VOLTAGE vs. CURRENT EXPERIMENTS		
	CHARGING TIME (minutes)	VOLTAGE AFTER 3-MINUTES WITH 5.08 ohm LOAD (volts)	OPEN CIRCUIT VOLTAGE (volts)	SHORT CIRCUIT CURRENT (amperes)	INTERNAL RESISTANCE (ohms)
801-11	3	0.90			
	2	1.03			
	3	1.24			
	3	1.96			
801-23	15	1.34			
	16	2.23	2.29	3.46	0.66
802-12	16	2.20	2.58	4.00	0.65
	30	2.20	2.61	3.58	0.89
802-13	64	2.33	2.55	6.56	0.39
802-23	16	0.92	0.58	1.43	0.40
802-28	16	1.83	2.07	3.52	0.59
804-9	32	2.04	2.54	3.45	0.74
806-18			2.54		
807-12	64	2.54	2.58	5.53	0.47

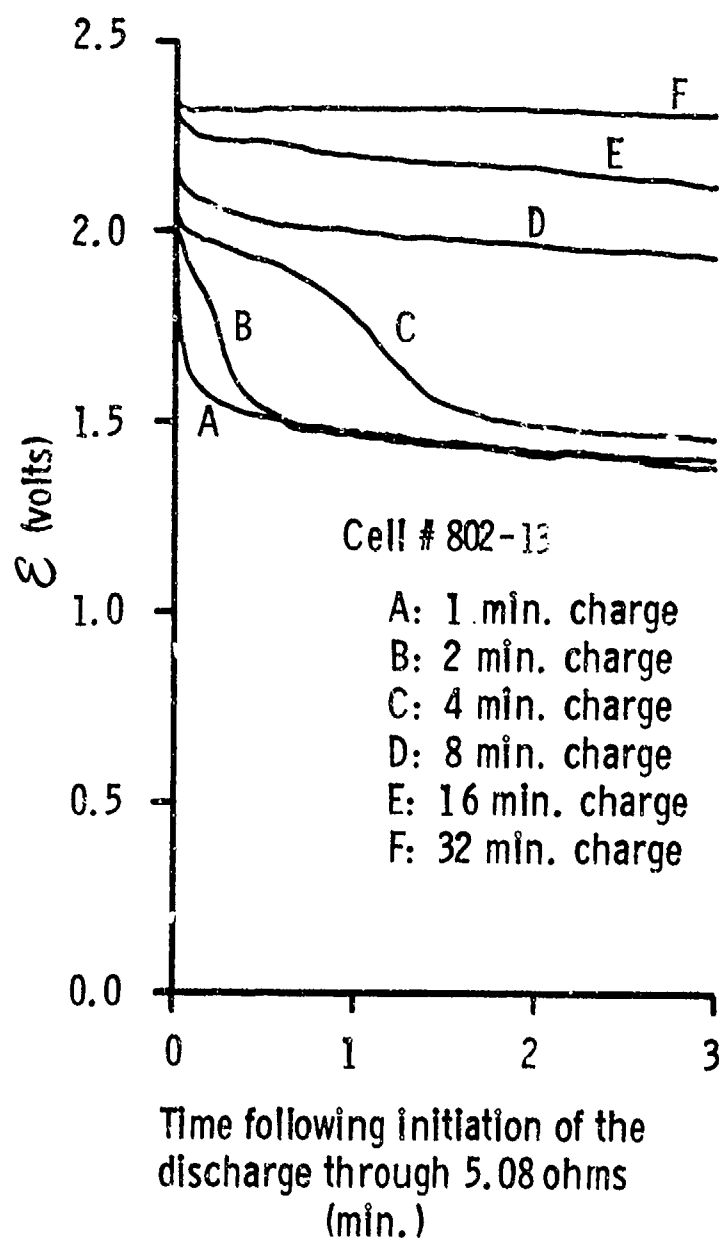


Figure 3. Cell Number 802-13: Results of Charge-Discharge Experiment

Further analysis of Figure 3 suggests that at least two processes were occurring during the discharge. The first process is represented by Curve A and has an estimated open circuit voltage of about 2 volts. The second process was important for the early portion of the discharge following the two minute charge (Curve B) and for a longer time following the four minute charge (Curve C). For charging times greater than four minutes (Curves D, E and F) it would appear that the second process dominated.

2. Cell Number 802-23. Instead of graphite, Cell Number 802-23 contained 1.5 grams of charcoal (decolorizing carbon) in the chlorine electrode compartment. The results of charge-discharge experiments are shown in Figure 4. For the first five cycles (Curves A - E) the cell behaved as expected. Note that the plateau is reached at a value slightly below 1.0 volt compared with typical graphite containing cells in which the plateau is reached at a value above 2.0 volts.

The sixth charge-discharge cycle (Curve F) gave unexpectedly poor results. No explanation for the apparent degradation between the fifth and sixth cycles can be offered at this time.

A voltage vs. current experiment, conducted following the sixth charge-discharge cycle, indicated that the cell was not ideal. The extrapolated open circuit voltage was 0.58 volts, which is clearly inconsistent with the results of the charge-discharge experiments.

Although Cell Number 802-23 raised numerous questions, its performance was so inferior to that of graphite containing cells that no more charcoal-containing cells were constructed.

3. Cell Number 802-28. The objective of experiments with Cell Number 802-28 was to study the effect of changing electrolyte composition. In this cell, the electrolyte contained 40 mole percent sodium chloride compared with the value for a saturated solution of 50 mole percent. Figure 5 shows the results for a typical voltage vs. current experiment. The behavior is found to be ideal, but the open circuit voltage is about one half volt less than that developed by cells having electrolytes saturated with respect to sodium chloride.

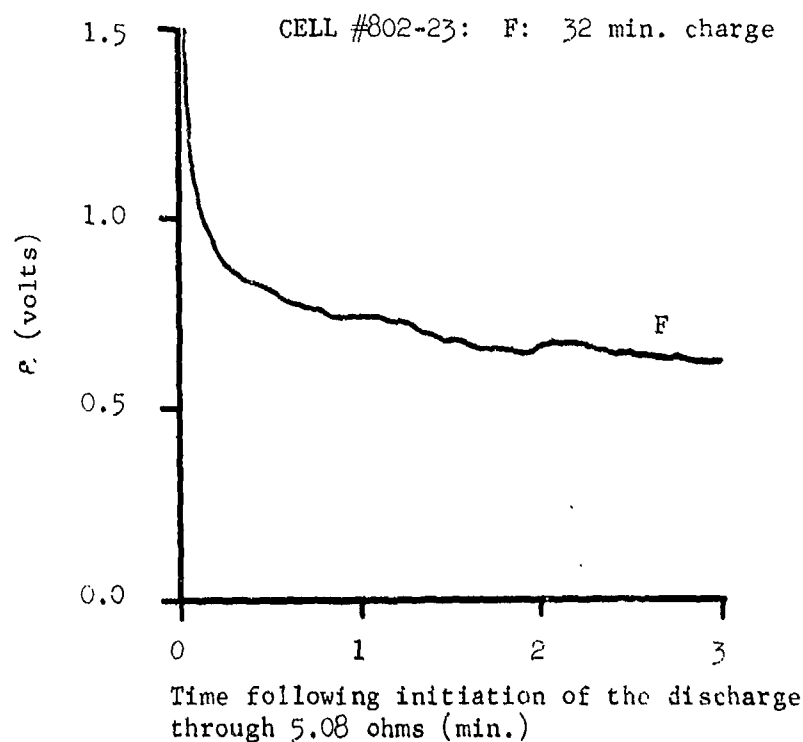
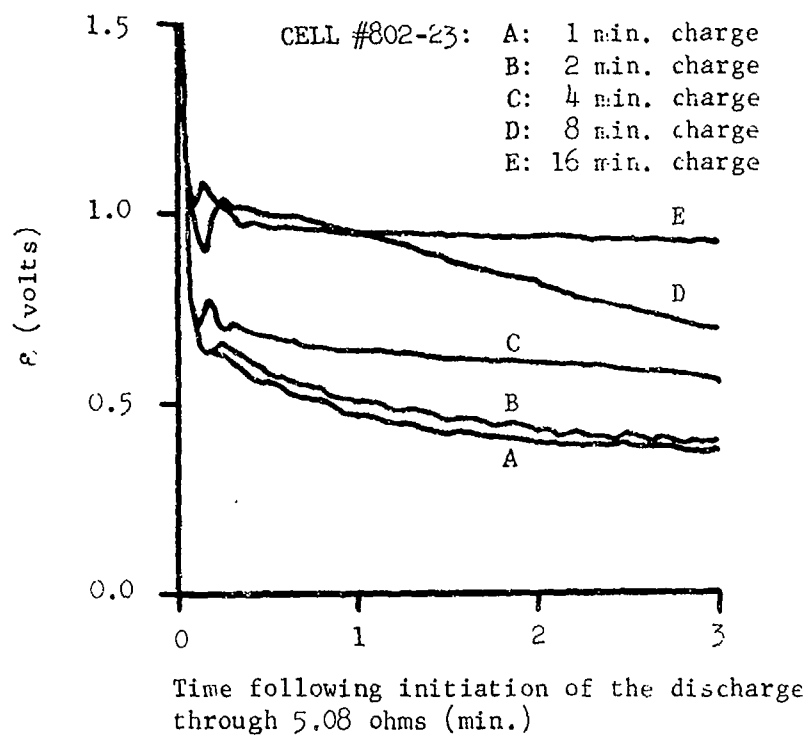


Figure 4. Cell Number 802-23: Results of Charge-Discharge Experiment

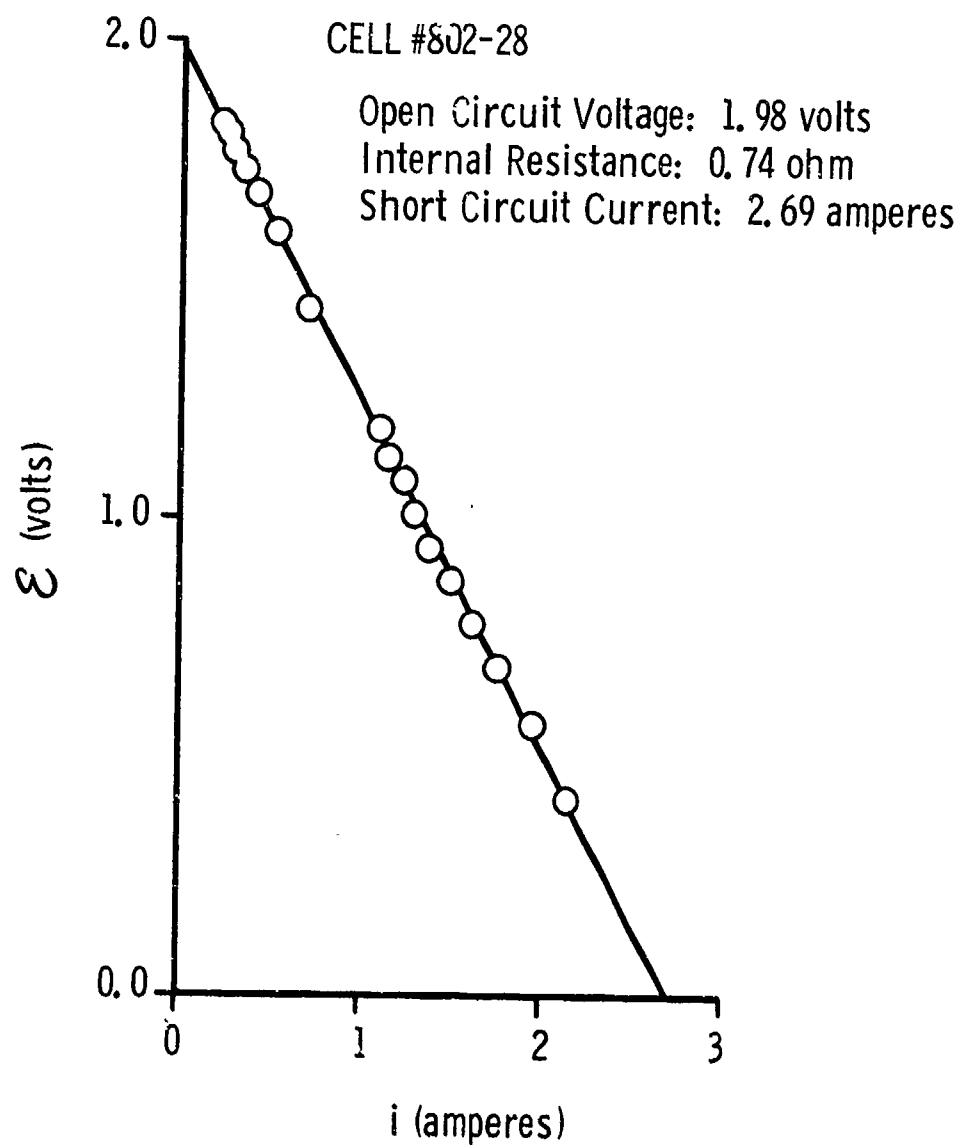


Figure 5. Cell Number 802-28: Results of Voltage vs Current Experiment

4. Cell Number 801-23. A series of charge-discharge experiments was conducted with Cell Number 801-23 using a graphite rod as the current collector in the chlorine electrode compartment. The final cycle in this series consisted of a 122 minute charge phase followed by a standard three minute discharge phase. Immediately after the termination of this discharge, the cell was removed from the constant temperature bath, allowed to cool to room temperature, and stored in a dry environment at room temperature for 60 hours. At the conclusion of this quiescent period, the cell was reheated. Prior to application of a load, the open circuit voltage stabilized at 2.50 volts. A prolonged discharge was then begun under a load of 5.08 ohms. Table 3 briefly summarizes the result of this experiment.

TABLE 3. CELL NUMBER 801-23: RESULTS OF PROLONGED DISCHARGE

TIME AFTER INITIATION OF DISCHARGE (minutes)	\mathcal{E} (volts)	i (amperes)
0	1.88	0.372
9	1.75	0.345
52	1.60	0.315
68	1.20	0.237
72	0.75	0.148
86	0.38	0.075
111	0.31	0.061

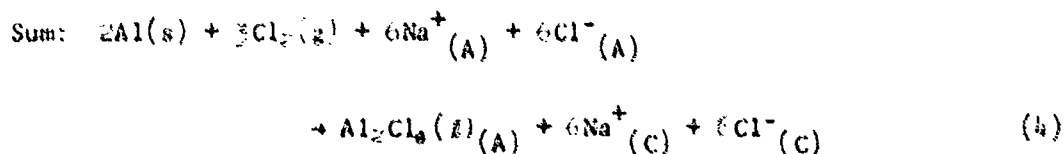
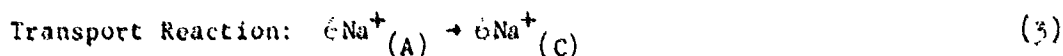
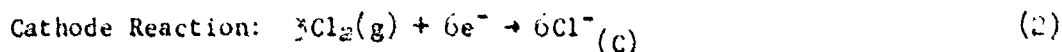
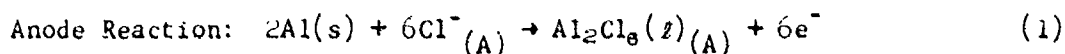
5. Analysis of the Graphite-Electrolyte Mixture. Since it was suspected that a compound might have been formed between the graphite and the chlorine, a sample of the graphite-electrolyte mixture was removed from Cell Number 801-23 just prior to cooling for the 60 hour quiescent period. This sample was quickly cooled, ground, and subjected to analysis by X-ray diffractometry. The dominant materials present were found to be graphite and NaAlCl_4 . There was also a small amount of AlCl_3 . $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and NaCl were missing and there

was no evidence for a chlorine-graphite compound. Although this experiment is indicative, it cannot be considered conclusive since X-ray diffractometry is not a particularly sensitive technique for the detection of trace amounts of compounds.

Discussion:

1. Expected Voltage. The observed open circuit voltage for the cells which have been described is about 2.55 volts. In order to place this value in perspective, it is necessary to examine the overall chemical reaction in terms of available thermodynamic and electrochemical data.

The overall chemical reaction can be written as follows:



In these equations, the subscripts "(A)" and "(C)" imply that the activities of the subscripted species are measured in the anode and cathode compartments, respectively.

The voltage for this reaction is then given by:

$$E = E^0 - \frac{RT}{6F} \ln \frac{(a_{\text{Na}^+_{(\text{C})}})^6 (a_{\text{Cl}^-_{(\text{C})}})^6 (a_{\text{Al}_2\text{Cl}_6(\text{l})_{(\text{A})}})}{(a_{\text{Na}^+_{(\text{A})}})^6 (a_{\text{Cl}^-_{(\text{A})}})^6 (f_{\text{Cl}_2(\text{g})})^3} \quad (5)$$

In this equation, the a's represent activities and the f stands for fugacity. The standard cell potential, E^0 , for this reaction depends

only on the free energy of $\text{Al}_2\text{Cl}_6(l)$ at the temperature of interest, and can be calculated from data given in the JANAF Thermochemical Tables.⁵ The following values were obtained by combining the enthalpy of formation, $\Delta H_f^\circ_{298.15}$, of Al_2Cl_6 with an interpolated value for the free energy function, $(G^\circ - H^\circ_{298.15})/T$, at 175°C .

$$\Delta G_f^\circ = 141.82 \text{ KCal/mole @ } 175^\circ\text{C}$$

$$E^\circ = 2.050 \text{ volts @ } 175^\circ\text{C}$$

It is apparent from equation (5) that a variety of factors enter into the calculation of the expected voltage of the cell. It is useful to consider three of these separately: (1) The fugacity of the chlorine, (2) the activity of the Al_2Cl_6 , and (3) the relative activities of the Na^+ and Cl^- ions.

a. Fugacity of Chlorine. For a cell in which chlorine gas is bubbled over an inert current collector, the fugacity of the chlorine can be estimated from the pressure. In the case of cells containing graphite, the fugacity can still be estimated provided the partial pressure of chlorine in equilibrium with the melt is known. Although precise pressure data have not been obtained, it has been observed that chlorine gas is released from the cathode compartment during electrical charging of the cells. Based on this observation, it will be assumed for the remainder of this discussion that the partial pressure of Cl_2 was equal to the prevailing atmospheric pressure at the altitude of this laboratory, i.e., approximately 600 torr. Equation (5) can then be reduced to:

$$E = 2.050 - \frac{141.82}{6F} - \frac{(a_{\text{Na}^+})^e (a_{\text{Cl}^-})^e (a_{\text{Al}_2\text{Cl}_6(l)})^1}{(a_{\text{Na}^+})^a (a_{\text{Cl}^-})^a} \quad (6)$$

at 175°C and 600 torr.

5. JANAF Thermochemical Data, The Dow Chemical Company, Midland, Michigan. The data for $\text{Al}_2\text{Cl}_6(l)$ are dated 30 June 1970. Note that, in the liquid phase, aluminum chloride is essentially completely dimerized.

b. Activity of Al_2Cl_3 . The influence of the activity of Al_2Cl_3 can be studied by assuming that the cell has no separator. Under these circumstances, the two electrode compartments have equal sodium ion activities and equal chloride ion activities, and Equation (6) can be further simplified to

$$\mathcal{E} = 2.045 - \frac{448.15R}{6F} \ln a_{\text{Al}_2\text{Cl}_3(l)} \quad (7)$$

at 175°C and 600 torr.

Fannin, King and Seegmiller have studied the structure of sodium chloride-aluminum chloride melts at 175°C .⁴ Using their data for $a_{\text{Al}_2\text{Cl}_3(l)}$, expected voltages for a cell without a separator have been calculated and are listed in Column 5 of Table 4. These data are shown graphically in Figure 6. Notice that the effect of increasing the mole fraction of AlCl_3 in the cell is a small decrease in the expected cell voltage.

c. Activities of the Na^+ and Cl^- Ions. The importance of the activities of sodium and chloride ions can best be illustrated by assuming that the cell has a separator, that the composition of the electrolyte in the aluminum electrode compartment is fixed by the presence of excess NaCl , and that the electrolyte in the chlorine electrode compartment has a variable composition. The expected voltages can be calculated using Equation (6) and the data of Fannin, King and Seegmiller.⁴ The results are summarized in Column 6 of Table 4 and displayed graphically in Figure 6. As expected, the cell voltage steadily increases as the concentration difference becomes more pronounced. The voltage increment due to the difference in electrolyte composition between the two electrode compartments can be readily obtained by subtracting the value in Column 5 from the corresponding value in Column 6 of Table 4.

2. Experimental Measurement of \mathcal{E}° . Because there is some uncertainty attached to the standard cell potential, \mathcal{E}° , for the

TABLE 4. EXPECTED CELL VOLTAGES FOR CELLS AT 175°C AND 600 TORR.

Mole Fraction AlCl_3	$\log_2 a_{\text{Al}_2\text{Cl}_6}(\lambda)(c)$	$\log_2 a_{\text{Cl}^-}(\text{c})$	$a_{\text{Na}^+}(\text{c})$	Cell Voltages Based on $\mathcal{E}^0 = 2.050$ volts		Cell Voltages Based on $\mathcal{E}^0 = 2.029$ volts	
				Without Separator (volts)	With Separator (volts)	Without Separator (volts)	With Separator (volts)
0.4980	-11.369	-2.399	0.5000	2.214	2.214	2.193	2.193
0.4985	-11.119	-2.523	0.5000	2.210	2.225	2.189	2.204
0.4990	-10.768	-2.698	0.5000	2.205	2.240	2.184	2.219
0.4995	-10.178	-2.992	0.5000	2.196	2.267	2.175	2.246
0.5000	-8.449	-3.856	0.5000	2.171	2.343	2.150	2.322
0.5005	-6.718	-4.722	0.5000	2.145	2.420	2.124	2.399
0.5010	-6.126	-5.019	0.5000	2.136	2.447	2.115	2.426
0.5015	-5.774	-5.196	0.5000	2.131	2.463	2.110	2.442
0.5020	-5.523	-5.322	0.5000	2.127	2.474	2.106	2.453
0.5030	-5.167	-5.502	0.5000	2.122	2.490	2.101	2.469
0.5050	-4.714	-5.732	0.5000	2.115	2.510	2.094	2.489
0.5070	-4.412	-5.886	0.5000	2.111	2.524	2.090	2.503
0.5100	-4.089	-6.054	0.5000	2.106	2.539	2.085	2.518
0.5200	-3.439	-6.398	0.4998	2.096	2.569	2.075	2.548
0.5300	-3.037	-6.619	0.4996	2.090	2.589	2.069	2.568
0.5400	-2.738	-6.791	0.4991	2.086	2.604	2.065	2.583
0.5500	-2.494	-6.937	0.4984	2.082	2.617	2.061	2.596
0.5600	-2.285	-7.066	0.4974	2.079	2.629	2.058	2.608
0.5800	-1.938	-7.293	0.4942	2.074	2.649	2.053	2.628
0.6000	-1.656	-7.491	0.4890	2.070	2.667	2.049	2.646
0.6200	-1.425	-7.664	0.4812	2.067	2.683	2.046	2.662
0.6400	-1.234	-7.817	0.4708	2.064	2.698	2.043	2.677
0.6600	-1.077	-7.952	0.4581	2.061	2.711	2.040	2.690
0.6800	-0.944	-8.071	0.4432	2.059	2.723	2.038	2.702
0.7000	-0.832	-8.180	0.4263	2.058	2.734	2.037	2.713

- Notes: 1. The data in this table are based on the results presented in Reference 4.
 2. At an AlCl_3 mole fraction of 0.4980 the melt is saturated with respect to NaCl .
 3. The data in Columns \mathcal{E} and \mathcal{E} are computed assuming that the electrolyte in the anode compartment remains saturated with respect to NaCl .

\mathcal{E} (VOLTS) BASED ON EXPERIMENTAL $\mathcal{E}^0 = 2.029$ VOLTS

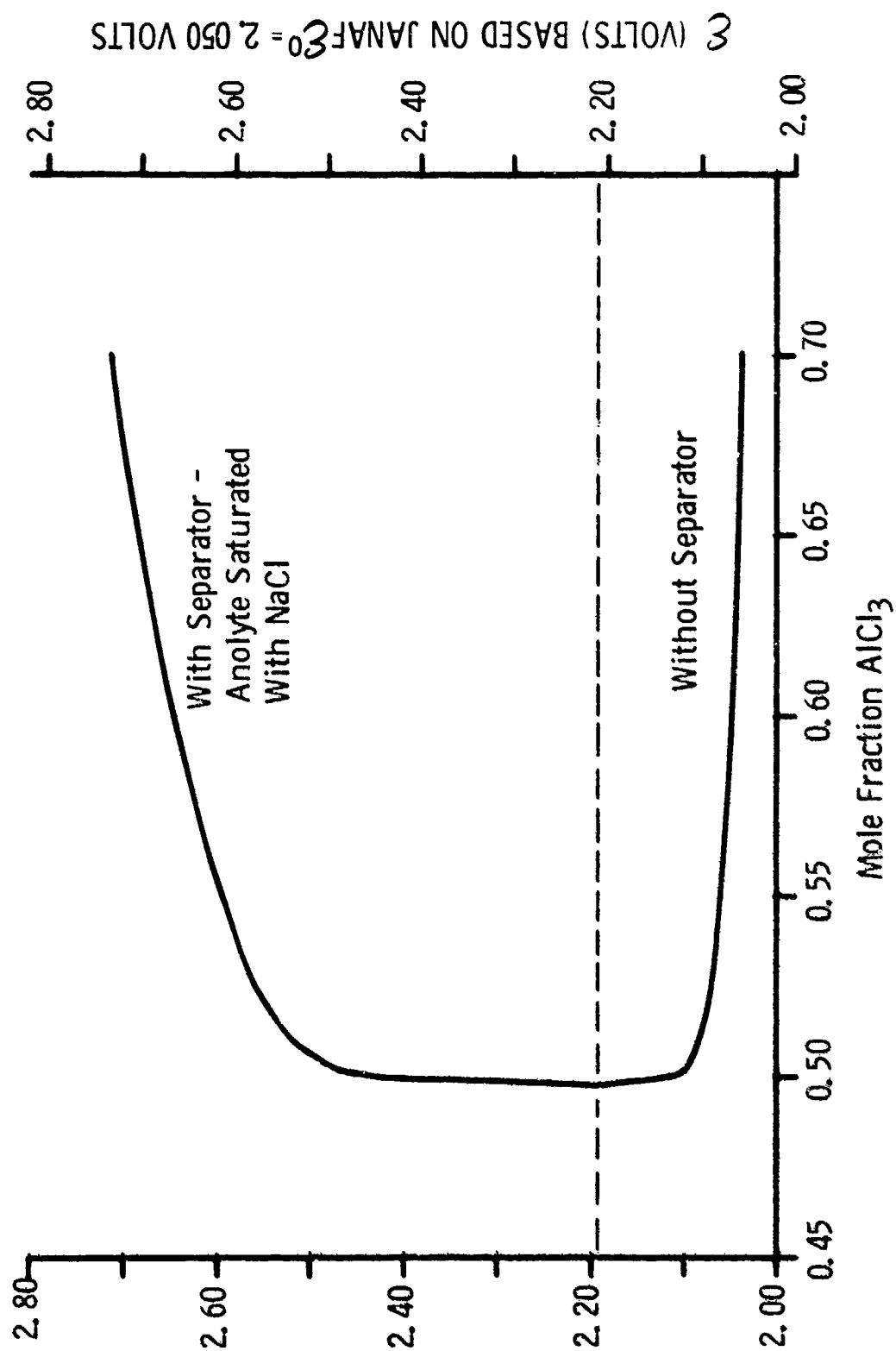


Figure 2. Expected Voltages for Cells with and without Separators at 175°C and 600 torr.

aluminum chloride formation reaction,



it was decided to determine this value experimentally. Direct measurement of \mathcal{E}° is difficult because of the fact that pure molten AlCl_3 is an insulator; the relatively high vapor pressure of AlCl_3 contributes additional experimental difficulties. By contrast, the formation reaction can be studied with ease in an electrolyte consisting of a saturated solution of NaCl in AlCl_3 . Rewriting Equation (5) for experiments carried out in a cell without a separator:

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{zF} \ln \frac{a_{\text{Al}_2\text{Cl}_6(l)}}{(f_{\text{Cl}_2(g)})^3} \quad (9)$$

Since the activity of Al_2Cl_6 is known from other experiments, \mathcal{E}° can be calculated from the experimentally determined voltage of a cell having no separator.

The cell used to establish \mathcal{E}° had an aluminum anode, an electrolyte consisting of a saturated solution of NaCl in AlCl_3 , and an ambient pressure Cl_2 gas electrode. Two different current collectors were used in the chlorine electrode compartment: A spectroscopic grade graphite rod and a tungsten wire. The cell was operated at $17^\circ \pm 1^\circ\text{C}$. Voltage measurements were made with a Data Technology Corporation digital voltmeter having an input impedance of 10^{10} ohms. The value obtained, 2.125 volts, was independent of the type of cathode current collector used, and remained stable indefinitely. During the period of measurements, the Cl_2 pressure varied with prevailing atmospheric pressure from 576.6 to 720.1 torr. This variation in pressure corresponds to a theoretical variation in measured voltage of ± 0.00015 volt. In the case of the graphite rod current collector, a period of approximately 48 hours elapsed before a stabilized voltage was achieved. In order to assure that the reversible value had in fact been obtained, a charging current of 20 milliamperes per square centimeter was applied for 30 minutes. At the conclusion of the charging period, the voltage rapidly stabilized at the previously observed

value. When the tungsten current collector was used, equilibrium was achieved in a much shorter period of time - - about 12 hours.

Using the value for the activity of Al_2Cl_3 reported by Fannin, King and Seegmiller⁴ (see Column 2, Table 4) and a chlorine fugacity of 0.766, a value of 2.029 volts is obtained for E° . Within experimental error, this value is equal to that calculated from the JANAF data.

Using the experimentally determined value for E° , a new set of expected voltages can be calculated using Equation (5) and the data of Fannin, King and Seegmiller.⁴ The results are summarized in Columns 7 and 8 of Table 4 and displayed graphically in Figure 6. The voltage increment due to the differences in electrolyte composition can be obtained by subtracting the value in Column 7 from the corresponding value in Column 8 of Table 4.

3. The Observed Voltages.

As indicated by Table 2, most of the experimental cells exhibited open circuit voltages between 2.5 and 2.6 volts. Since these observed open circuit voltages are substantially higher than the voltage expected for a cell without a separator (see Columns 5 and 7 in Table 4), it can be concluded that there was a significant concentration difference between the electrolytes in the two electrode compartments. The magnitude of this concentration difference is indoubt since the value of the standard cell potential is not known with certainty; two cases (i.e., $E^\circ = 2.057$ volts and $E^\circ = 2.029$ volts) are treated in detail in Table 4.

The concentration difference is created during the electrical charging of the cell. Two factors make the development of the concentration difference possible: (1) Prior to electrical charging, the electrolyte in the chlorine electrode compartment, although saturated in NaCl, contains no excess NaCl; and (2) sodium ion is the principal ionic charge carrier. During charging, sodium ion migrates from the

chlorine electrode compartment into the aluminum compartment thus depleting the NaCl content in the chlorine electrode compartment and creating the concentration difference between the two compartments.

The charge-discharge experiments are indicative of the fact that a concentration difference is developed during charging. Figure 3 suggests that at least two processes are important during the electrical charging process. The process which involves development of the concentration difference seems to be first evident during the two minute charge (Note the step wise discharge behavior suggested by Curve B and clearly displayed by Curve C.) and to be increasingly important as the charging time is increased.

The experiment with Cell Number 802-28, which had an electrolyte containing only 40 mole percent NaCl, further supports the contention that a concentration difference is developed during charging. Although small concentration differences were doubtless developed during electrical charging of Cell Number 802-28, the aluminum electrode compartment could not achieve an electrolyte composition saturated with respect to NaCl. As a consequence, a large enhancement of the open circuit voltage would not have been observed. In fact, the largest open circuit voltage observed for this cell was 2.25 volts.

b. Nature of Cathode.

It is of interest to speculate as to the nature of the cathode in these cells. The following facts can be assembled:

a. The current which can be drawn from a cell is essentially independent of the surface area of the tungsten wire. Consider, for example, Cell Number 802-12B. Using a straight tungsten wire current collector with a surface area of 1.2 cm^2 , the short circuit current was 3.58 amperes; thus the current density at the tungsten wire was 3.0 amperes/ cm^2 . By comparison, Cell Number 804-9 used a spiral tungsten wire current collector having an effective surface area of 5.27 cm^2 ; the short circuit current for this cell was virtually identical with that for Cell Number 802-12B.

b. Graphite and charcoal behave very differently when in the chlorine electrode compartment. In the case of graphite, the cell behaves ideally and the measured open circuit voltage equals the value obtained by extrapolation of the voltage vs. current curve. By contrast, cells, containing charcoal do not behave ideally, and the voltages obtained are significantly lower than those observed with graphite-containing cells.

c. Tungsten/chlorine gas electrodes behave very differently from tungsten/chlorine/graphite paste electrodes. This fact has been demonstrated by studying the behavior of a tungsten wire electrode in an electrolyte saturated with chlorine gas at a pressure of two atmospheres. In this system, the tungsten electrode becomes severely degraded when the cell is loaded such that the voltage drops below about 1.5 v. The current density at which the degradation begins is about 10 ma/cm², based on the effective area of the tungsten cathode.

Based on these facts, it seems very probable that the powdered graphite, rather than the tungsten wire itself, is acting as the cathode. Moreover, the electronic conductivity of the graphite is most likely important and assures efficient transport of electrons from the tungsten wire current collector to the electroactive sites on the surfaces of the graphite particles.

d. Temperature Dependence. The purpose of the experiments with Cell Number 807-12 was to obtain data which could be compared directly with "expected" voltages calculated for cells at 175°C. Within the limits of experimental uncertainty, Cell Number 807-12 behaved in the same manner as the other cells at 200°C.

e. Possible Applications. A variety of possible applications can be imagined for the cell described in this report. Additional data will have to be accumulated, however, before it can be said that the cell is indeed suitable for any particular application.

There are two characteristics of the cell which seem to warrant further development of the system:

- a. The ability of the cell to deliver large currents, and
- b. The ability of a cell cooled to room temperature to store its energy for a significant length of time.

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